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(71) Applicant(s)
Chinese Petroleum Co.

(Incorporated in Taiwan)

No 83 Sec 1 Chung Hua Rd, Taipei, Taiwan

(72) Inventor(s)
Tzong-Bin Lin
Tse-Chaun Chou
Kun-Yung Tsai

(74) Agent and/or Address for Service
Mewburn Ellis
York House, 23 Kingsway, LONDON, WC2B 6HP,
United Kingdom

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U1S S1511

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GB 1601715 A      GB 1538330 A      GB 1440789 A
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(58) Field of Search
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(54) **Eggshell catalyst and process for preparing of the same**

(57) Disclosed is a new method for preparing supported metal catalysts with eggshell active metal profile. The organometallic compounds with metal as Pd, Ni, Co, Mo, Cu, Pt, Fe, Ag, Ir, Pb, Ti, Sn, V, and Zn, etc., are dissolved in a pure organic solvent, such as benzene, toluene, xylene, methanol, ethanol, and tetrahydrofuran (THF), etc., and/or an organic solvent mixture thereof. The catalyst precursors (i.e., the reactive metal of the prepared organic or inorganic metal concentrated solution) are carried to the surface of MgO, Al₂O₃, SiO₂, TiO₂, ZrO₂, zeolite, active carbon, and polymer support by wet impregnation and/or spray method. The metal concentration profile and metal loading can be precisely controlled by choosing suitable solvent and/or operation conditions.

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Weight content of Pd metal, wt%

Fig.1

Thickness of Pd metal eggshell r/R

Fig.2

Thickness of Pd metal eggshell r/R

1mm

Fig.3

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Fig.4

Fig.5

(a)

(b)

Retention Time(min)
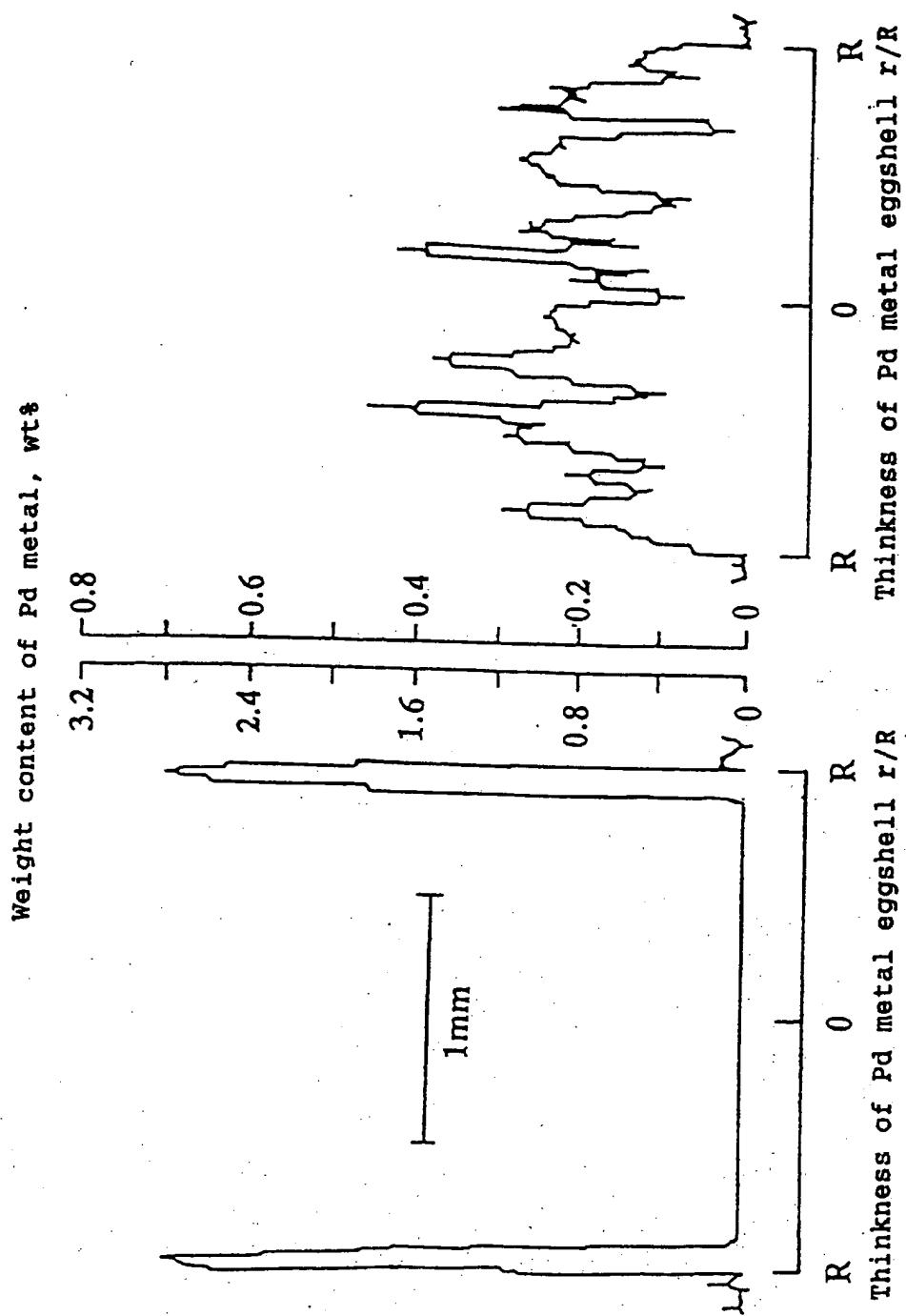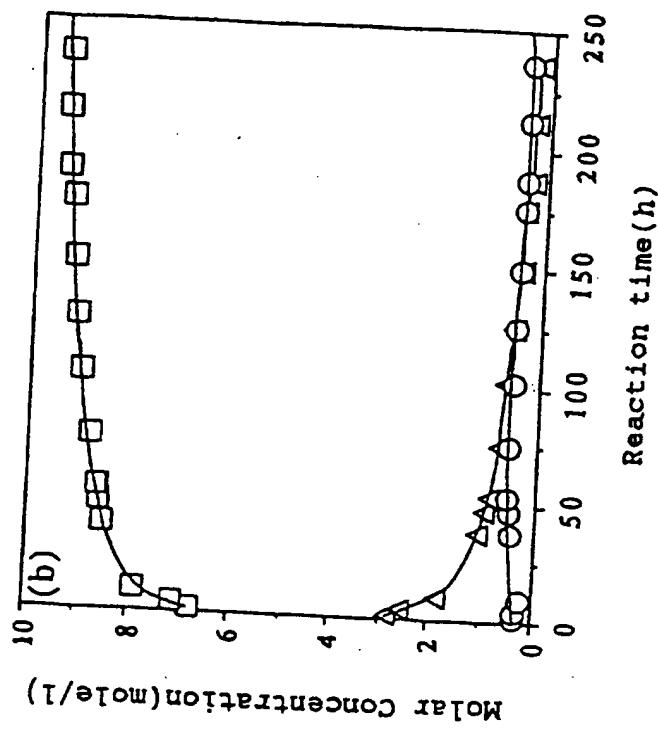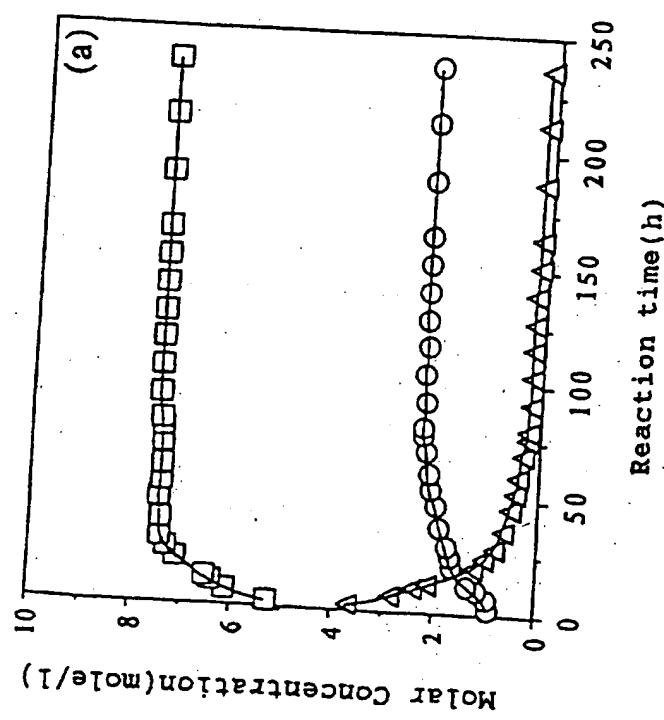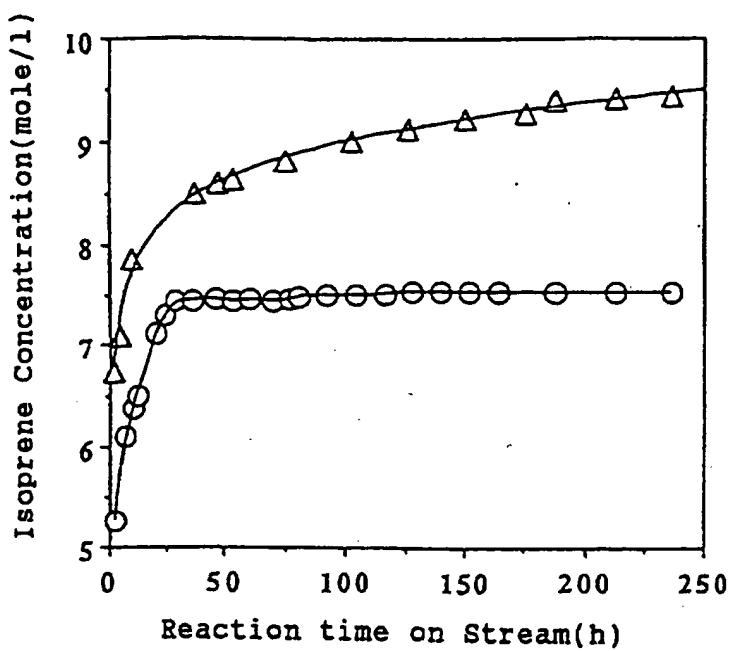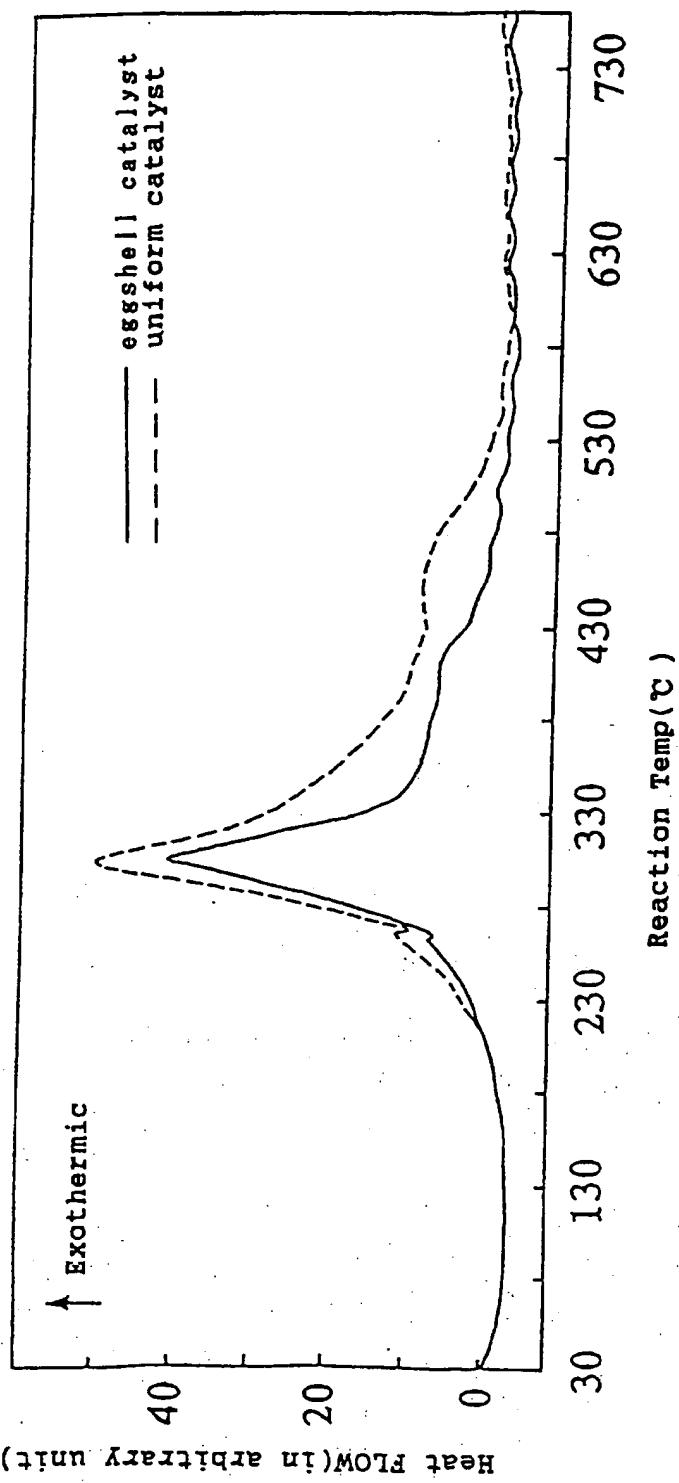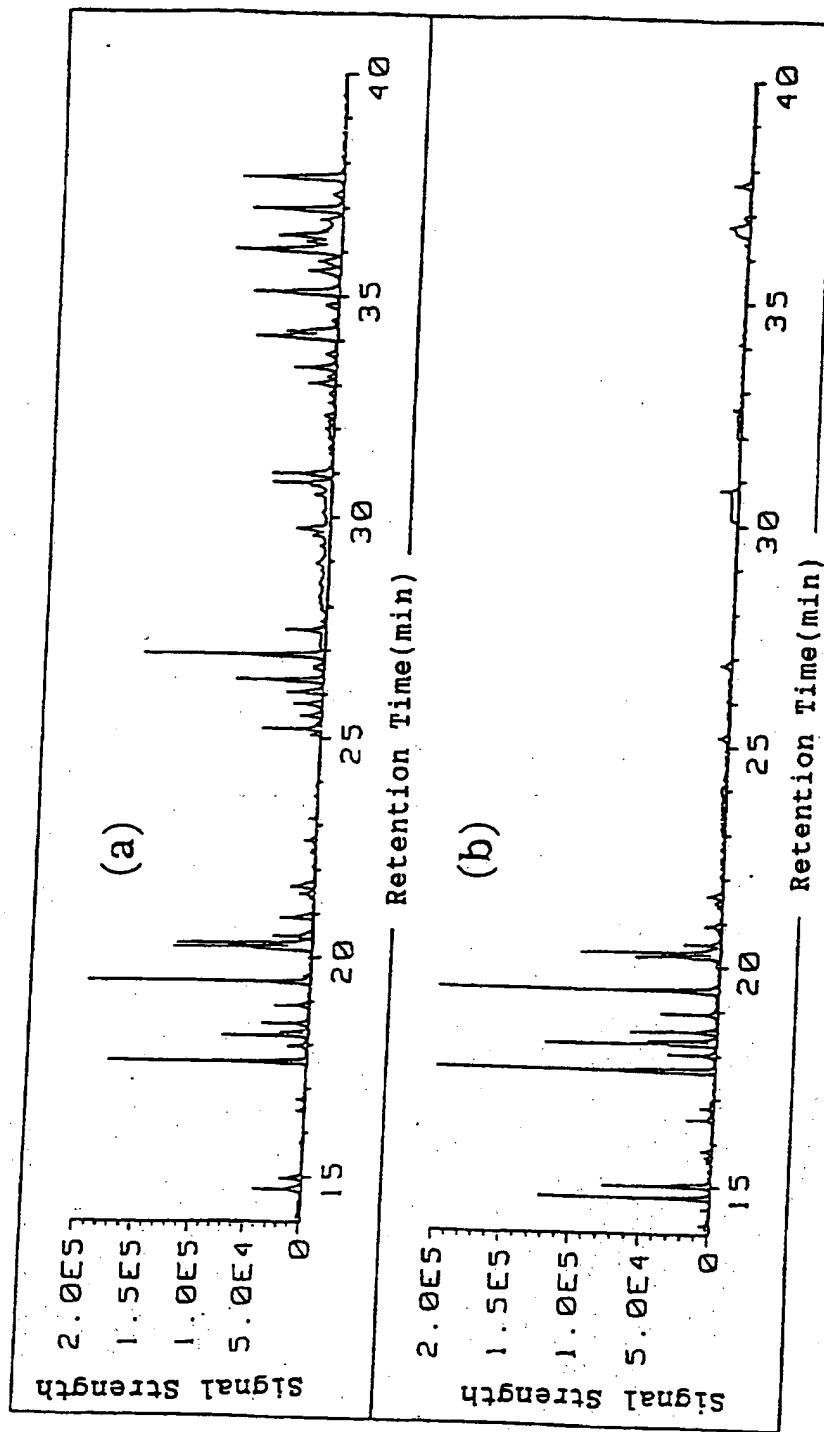
Fig.6
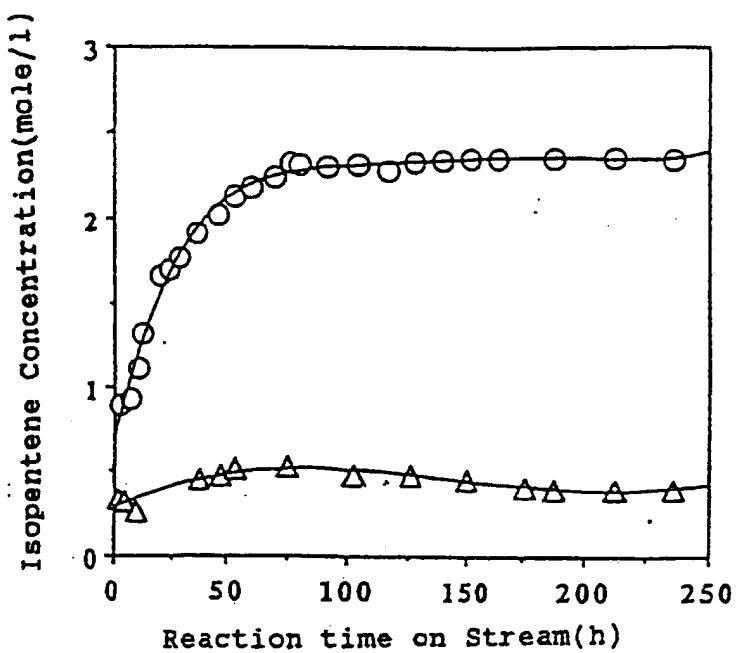
Fig.7
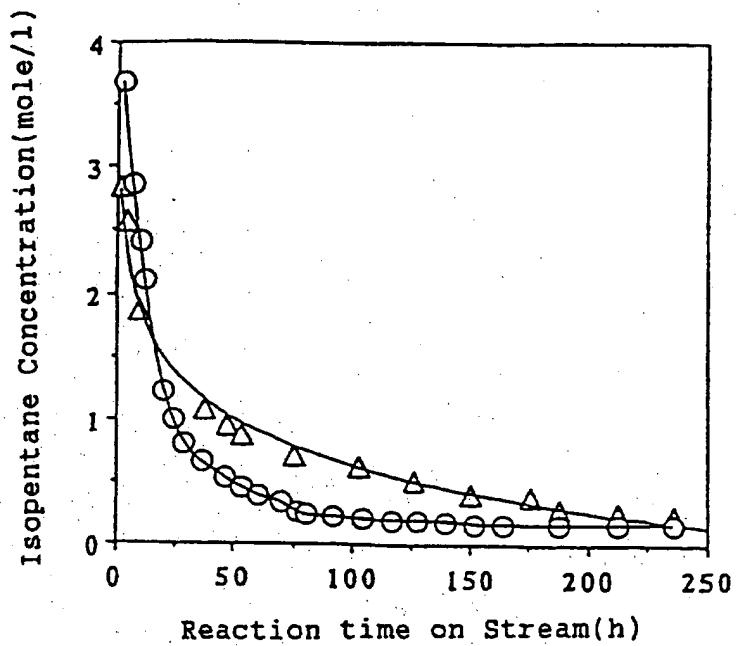


Fig.8
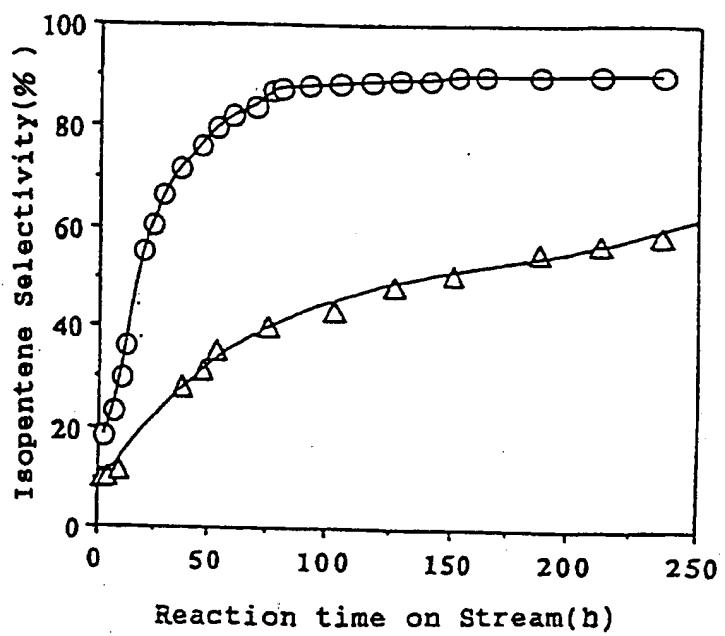
Fig.9
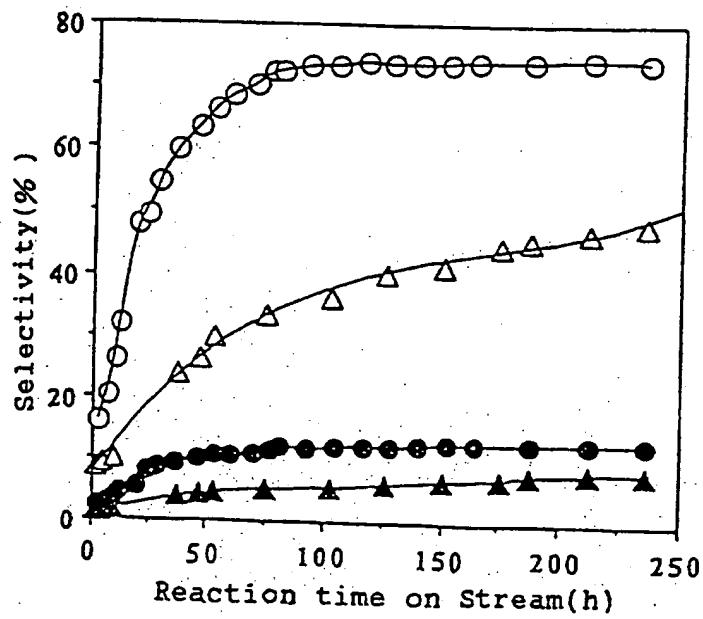


Fig.10

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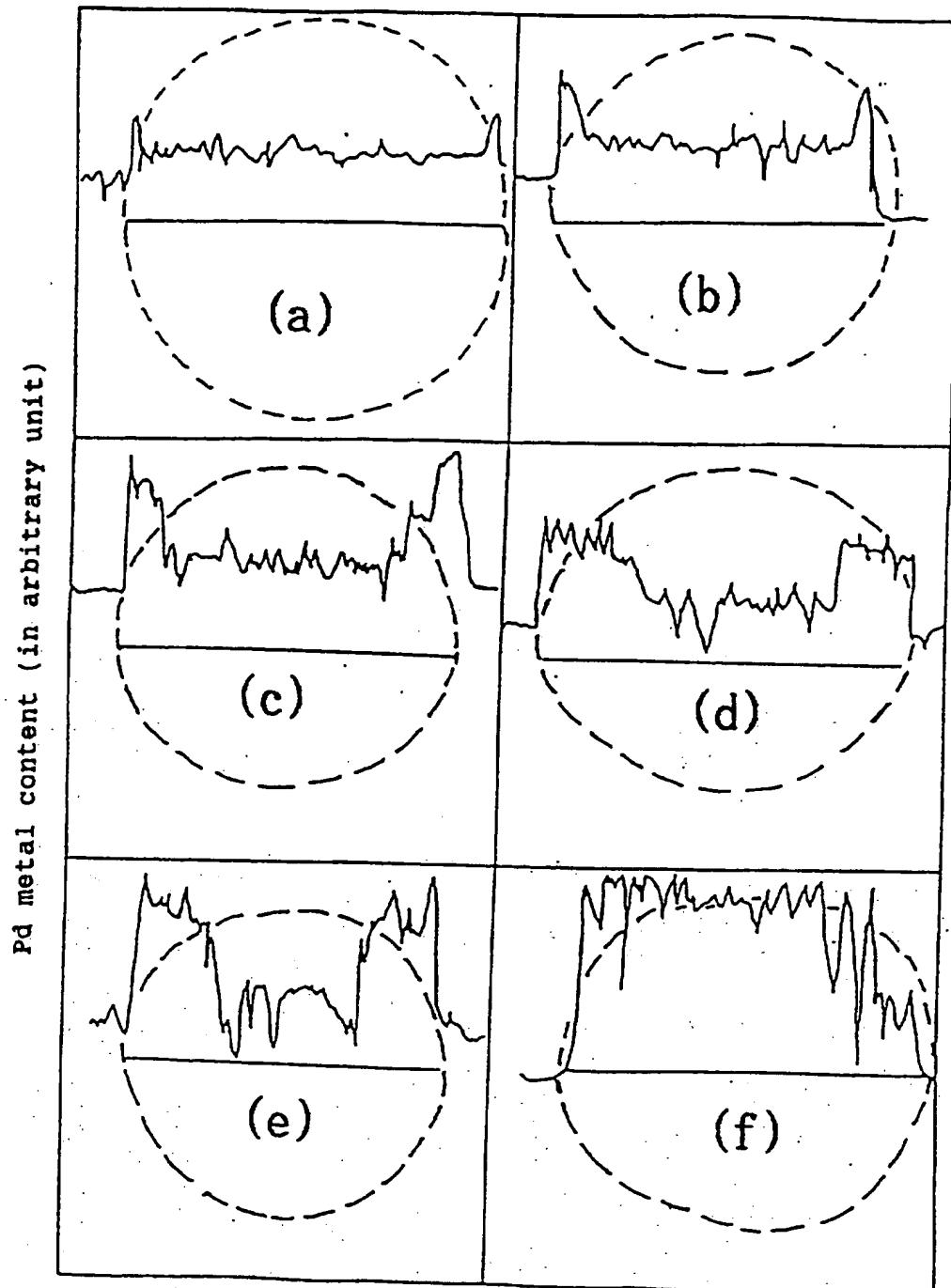
Radius site of sopport particles, r/R

Fig.11
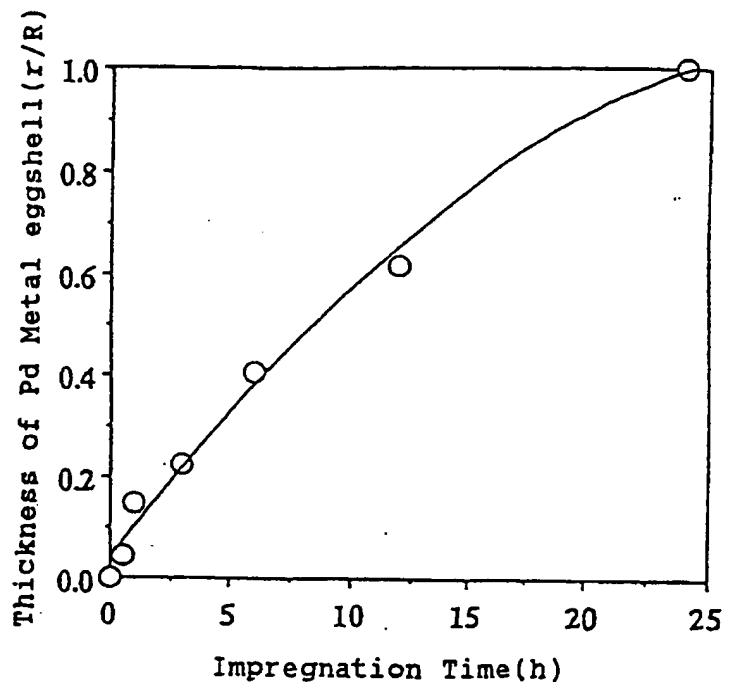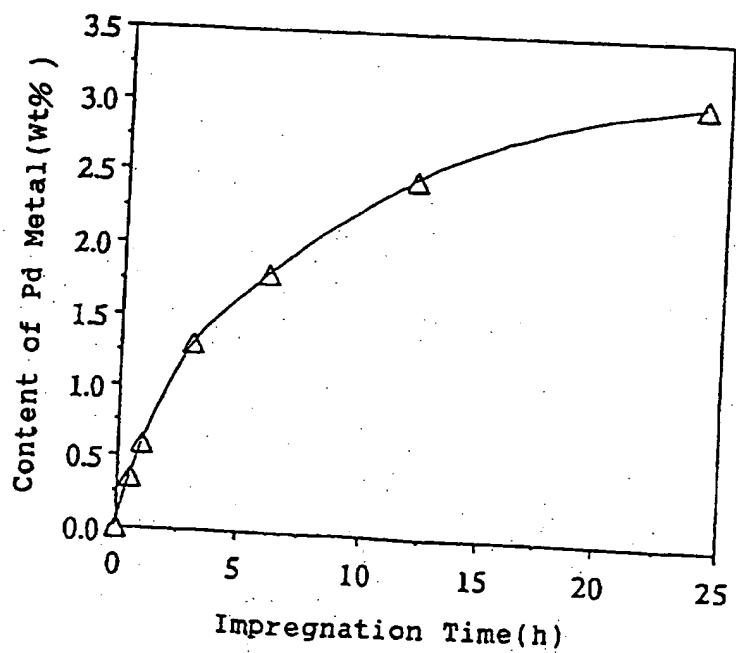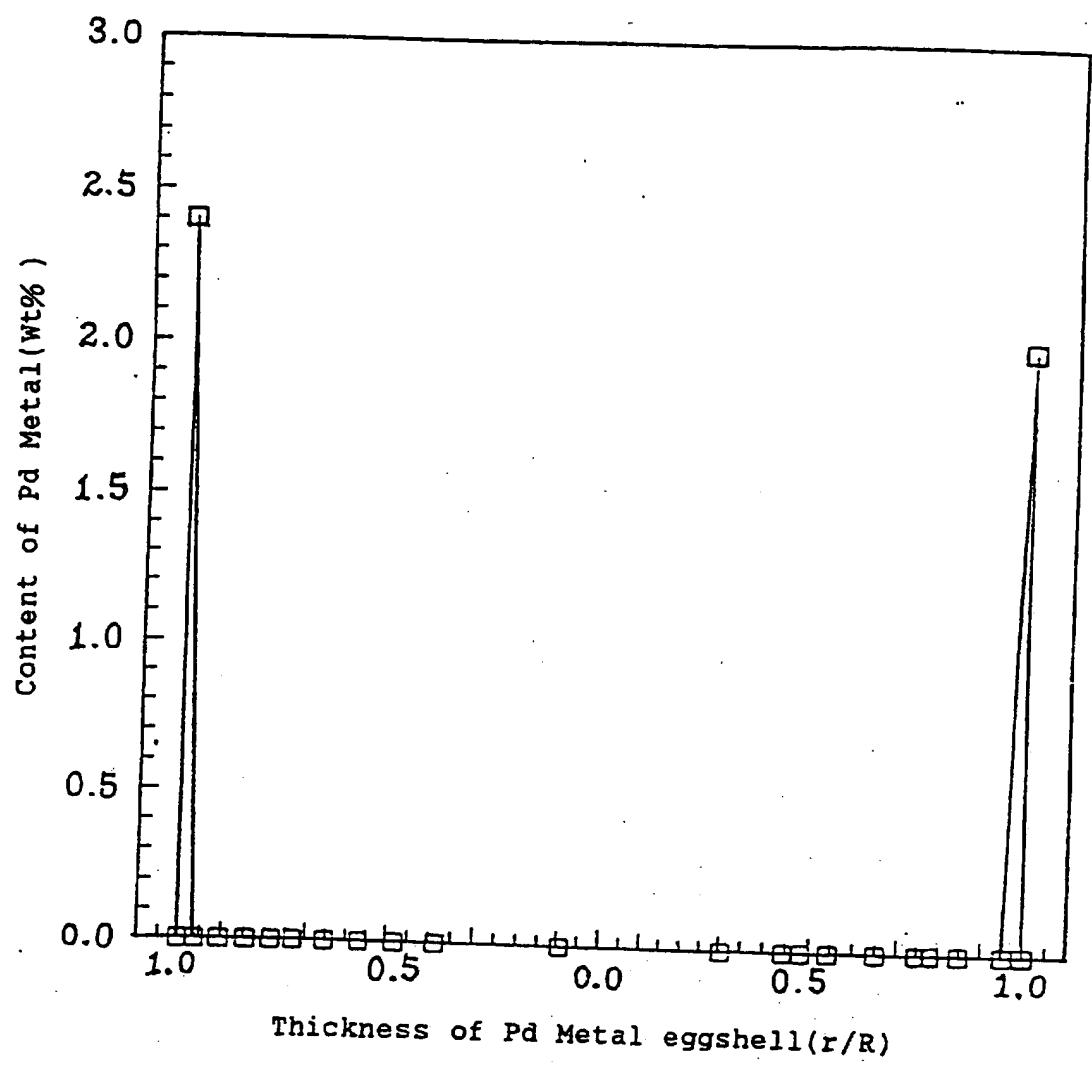
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Fig.12



Fig.13

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Fig.14
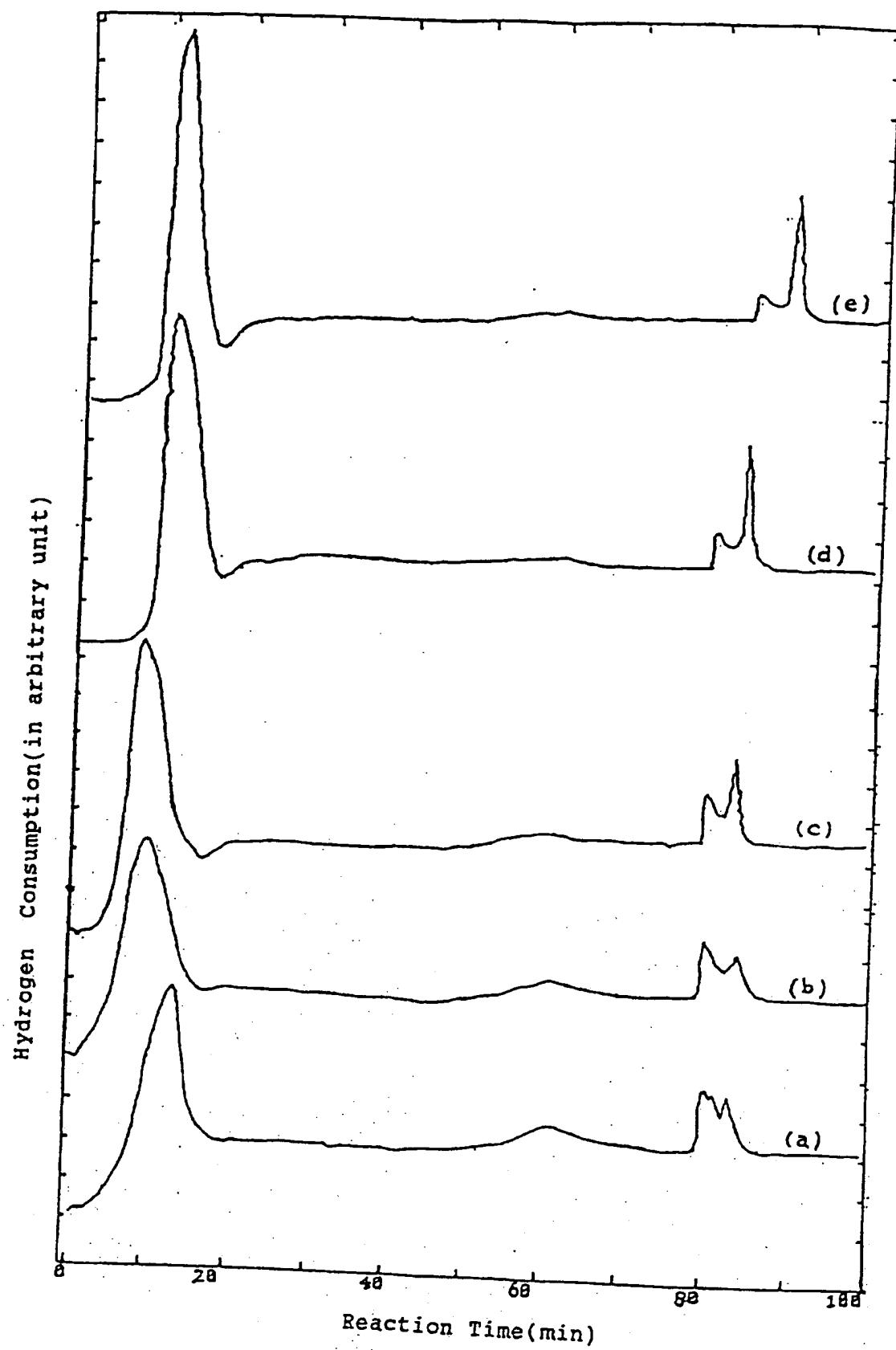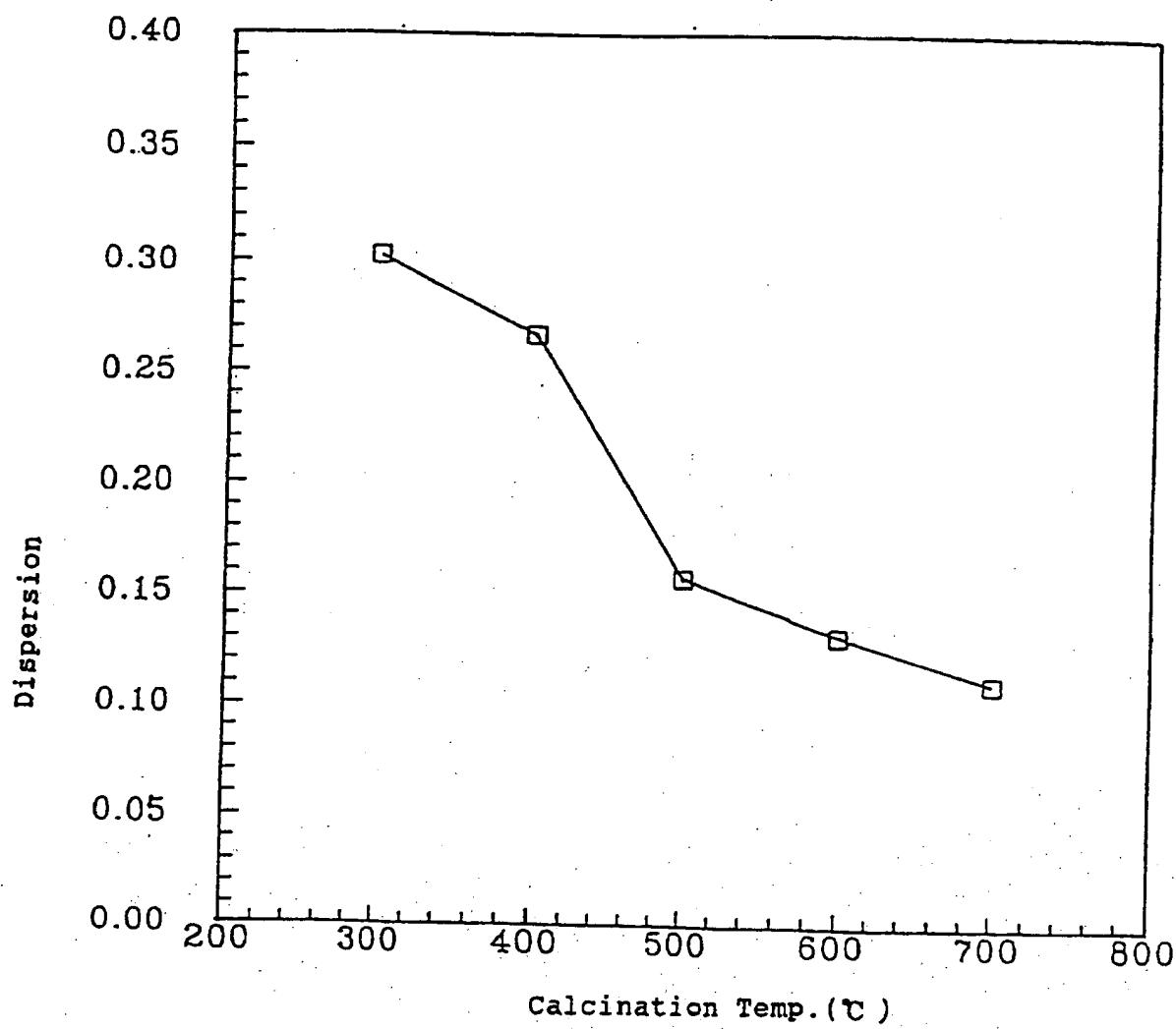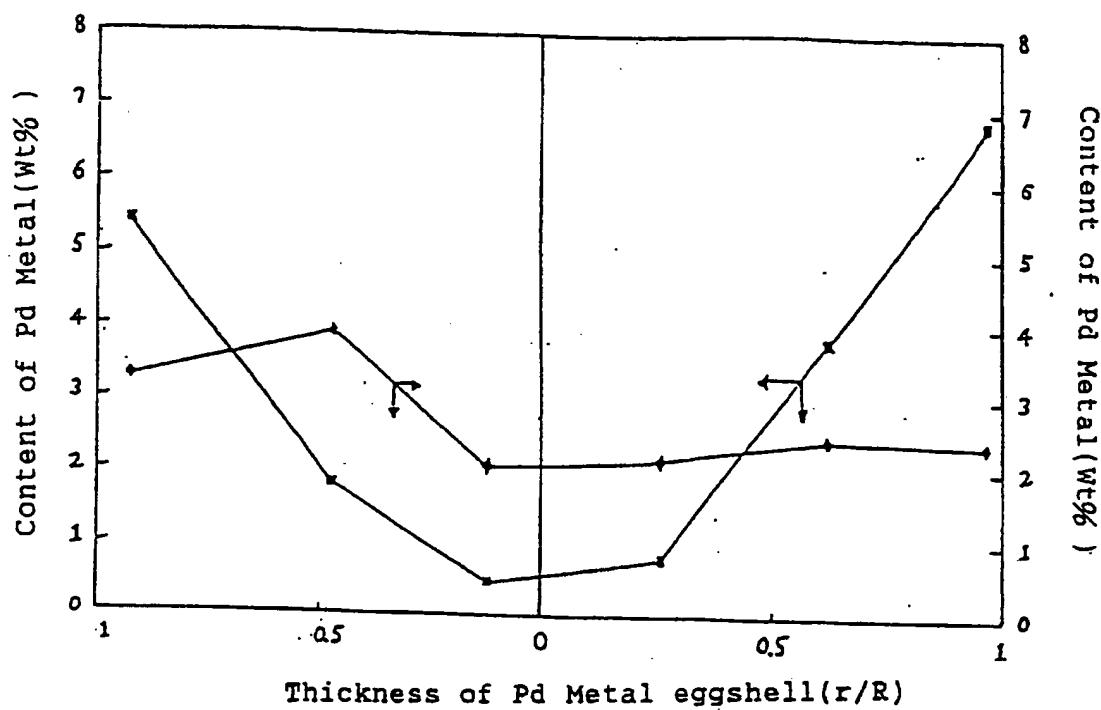
Fig.15

Fig.16

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Fig.17(a)



Thickness of Pd eggshell(r/R)  Thickness of Pd eggshell(r/R)
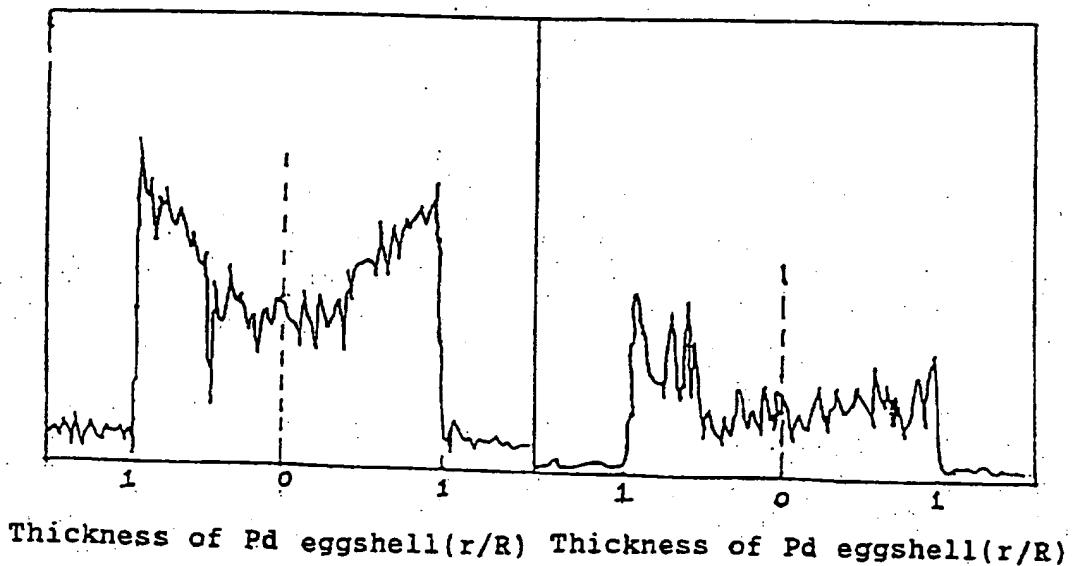
Fig.17(b)

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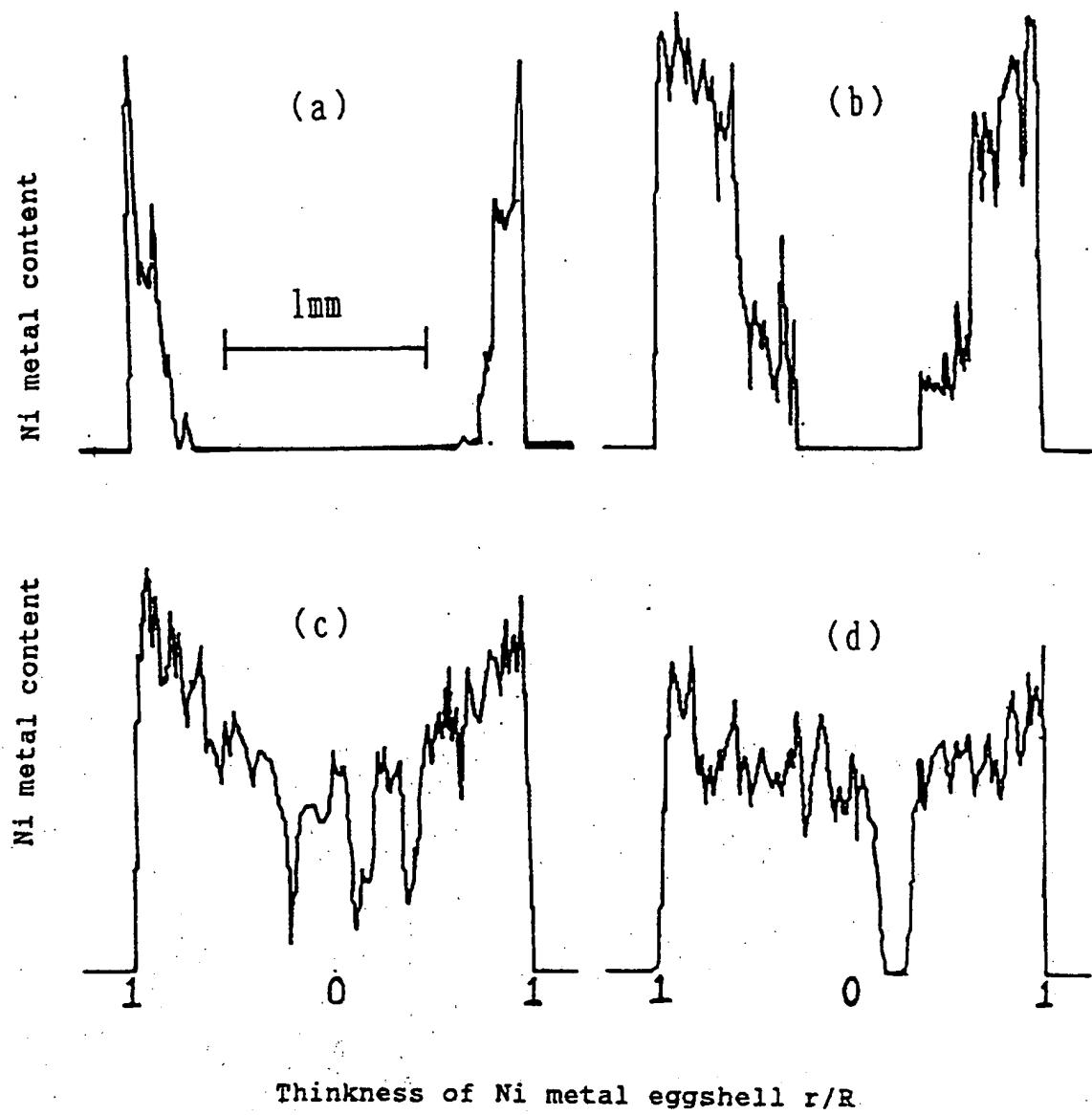
**Fig.18**

Eggshell Catalyst and Process for Preparation of the Same

The present invention is related to an eggshell catalyst and process for preparation of the same, to precisely control the thickness of single- or multiple-metal eggshell of the finished catalyst and some important properties, such as, metal content and metal dispersion.

The porous supports with active metals non-uniformly distributed have been widely studied and applied in petroleum refining and petroleum chemical industries currently. They have been theoretically and experimentally proved to own adventages of improving yield and selectivity, reducing thermal sensitivity, resisting poisoning and activity decay, and increasing wear-resistance, etc. According to the description in Ind. Eng. Chem. Prod. Res. Dev. 1981, Vol.20, p439, non-uniformly active metal distribution can be classified into four types.

1. Metal is uniformly distributed, which is usually used in reactions with catalyst having fair activity and no mass transfer resistance.

2. Metal is distributed on the outer layer of the support (with eggshell shape), which is usually used in fast reactions and capable of improving the selectivity and yield of the desired products.

3. Metal is distributed inside the support (with eggyolk shape), which is usually used in a fluidized bed or a moving bed and the outer layer of the catalyst may easily show wear or poisoning.

4. Metal is distributed between eggshell shape and yolk shape, as egg white shape, which is suitable for a reaction range between those conducted by the eggshell- and the eggyolk-shaped catalyst, with mass transfer resistance inside the particle and wear or poisoning easily shown on the outer layer.

Currently, eggshell catalysts have been widely employed in the industrially selective hydrogenation, such as, acetylene's hydrogenation to

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ethylene, dienes' hydrogenation to monoenes in gasoline cracking, etc., selective isomerization, such as, $\alpha$-olefins' conversion to $\beta$-olefins, etc., selective oxidation, for example, ethylene's reaction to ethyloxides, oxidation of $SO_2$, oxidation of CO, etc. The yield and selectivity of the desired products of the above reactions can be increased by using eggshell catalysts. In particular for consecutive reactions A →B →C, it is verified (see Chem. Eng. Sci., 27, (1972) 227; Supra, 29, (1974) 1473) that the yield and selectivity of product B can be increased by eggshell catalyst. According to the disclosure from J. of Chem. Eng. of Japan, 22(3), (1989) 287, it is verified that the order of ethylene selectivity in the selective hydrogenation of acetylene with major product of ethylene depends upon the metal distribution on catalyst $Ni/Al_2O_3$ as the following:

eggshell of thin layer > eggshell of thick layer > uniform distribution > eggyolk distribution

Up to now, the manufacturing of non-uniformly distributed metal on support stated in the patents and literatures is as follows.

$H_2PtCl_6$ and citric acid are co-impregnated to produce various non-uniformly distributed Pt on spherical alumina support and the experimental error of reproducibility is about 10% [see USP Nos. 3,259,454 and 3,259,589 (July 5, 1966); E.R. Becker etal., in "Preparation of catalysts Ⅱ:Proceedings of the 2nd international Sympogereous Catalysts", Elsevier, Amsterdam, 1979, P159]. The precursors of $CrO_3$, $(NH_4)_2Cr_2O_7$, and $Cu(NO_3)_2$, etc. are used by means of various impregnation technologies to produce non-uniformly distributed Cr and Cu metal in different state on spherical $Al_2O_3$ support [see J. Catal., 43, (1976) 200]. Platinum can be modified into nine different states non-uniformly distributed on spherical $Al_2O_3$ support by adding salts of HCl, NaBr, and the like to an impregnating solution of $H_2PtCl_6$ [see J. Catal., 63, (1980) 425].

According to the above-mentioned reports, to manufacture non-uniformly distributed metal on support needs to use inorganic metal salts and other salts and the metal thickness and site are controlled by means of pH value adjusting. These methods have disadvantages as the follows. 1. The anions of

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the inorganic salts can be retained on the support, which needs to be removed by high temperature calcination. Some anions, such as $Cl^-$, $SO_4^{-2}$, and the like, are not easily to be removed. If the catalyst is reactive at metallic state by a reduction of hydrogen, these anions could react with hydrogen to form HCl and $H_2SO_4$ which will cause acidic corrosion of equipment piping. 2. It is very difficult to control the metal thickness and weight percentage of the eggshell-shaped catalyst by the methods disclosed in the prior arts.

Accordingly, the present invention is a process for preparation of eggshell metal catalysts. Said process utilizes organo- or inorgano-metallic compounds, in which the metal preferably comprises Pd, Ni, Co, Mo, Cu, Pt, Fe, Ag, Ir, Pb, Re, Ti, Sn, V, and Zn, etc., by dissolving in organic solvents, such as aromatic solvents, e.g., toluene, benzene, and xylenes, alcohols, eg. methanol, and tetrahydrofuran (THF), etc. or in a variety of mixtures thereof under heating or at ambient temperature. The active metal in the prepared organo- or inorgano-metallic concentrate solution is attached to a support by wet impregnation or spray method, in which the support comprises $Al_2O_3$, $SiO_2$, zeolite, $TiO_2$, $ZrO_2$, MgO, active carbon, polymer or the mixtures thereof. The process of preparation according to the present invention can employ different operating variables, for example, $Al_2O_3$ maybe calcined at different temperatures for changing its surface area and acidity, or, the impregnated catalyst may be calcined at different temperatures, or the type and the concentration of the impregnating solution may be varied, etc. so as to precisely control the thickness of single- or multiple-metal eggshell of the finished catalyst and some important properties, such as, metal content and metal dispersion.

The following examples in combination of the drawings provide a better illustration of the present invention but do not limit its scope which is described in enclosed claims.

Fig. 1 shows a result of Pd metal distribution from EPMA (electron probe microanalyser) of a uniform catalyst (X-axis : thickness of Pd metal eggshell, r/R; Y-axis : weight content of Pd metal, wt%).

Fig. 2 shows a result of Pd metal distribution from EPMA of an eggshell catalyst (X-axis : thickness of Pd metal eggshell, r/R; Y-axis : weight content of Pd metal, wt%).

Fig. 3 shows two plots of reaction mixture composition vs. reaction time on stream for (a) eggshell catalyst (b) uniform catalyst at reaction temperature =44°C, pressure=30 atm, weight hourly space velocity (WHSV) of liquid = 18h$^{-1}$, molar ratio of $H_2$/isoprene =2.262 ( $\square$:isoprene, $\bigcirc$:isopentene, $\triangle$:isopentane).

Fig. 4 shows a plot of isoprene concentration vs. reaction time on stream of two catalysts at reaction temperature = 44°C, pressure =30 atm, WHSV of liquid = 18h$^{-1}$, molar ratio of $H_2$/isoprene =2.262 ($\bigcirc$: eggshell catalyst, $\triangle$:uniform catalyst).

Fig. 5 shows a DSC analysis for the coke precursor of two spent catalysts ( ———— :eggshell catalyst, -------:uniform catalyst).

Fig. 6 shows a spectrum of GC/mass analyser of the coke precursor of two types of spent catalysts (a) uniform catalyst and (b) eggshell catalyst.

Fig. 7 shows a plot of major product isopentene concentration vs. reaction time on stream of two catalysts at reaction temperature=44°C, pressure = 30 atm, WHSV of liquid =18h$^{-1}$, molar ratio of $H_2$/isoprene =2.262 ( $\bigcirc$:eggshell catalyst, $\triangle$:uniform catalyst).

Fig. 8 shows a plot of undesired isopentane concentration vs. reaction time on stream of two catalysts at reaction temperature=44°C, pressure=30 atm, WHSV of liquid =18h$^{-1}$, molar ratio of $H_2$/isoprene =2.262 ($\bigcirc$:eggshell catalyst, $\triangle$:uniform catalyst).

Fig. 9 shows a plot of isopentene selectivity vs. reaction time on stream of two catalysts at reaction temperature =44°C, pressure= 30 atm, WHSV of liquid =18h$^{-1}$, molar ratio of $H_2$/isoprene =2.262 ($\bigcirc$:eggshell catalyst, $\triangle$:uniform catalyst).

Fig. 10 shows a plot of 2-methyl-1-butene(2M1B) and 2-methyl-2-butene (2M2B) selectivity vs. reaction time on stream of two catalysts at reaction temperature =44°C, pressure =30 atm, WHSV of liquid =18h$^{-1}$, molar ratio of $H_2$/isoprene =2.262 ($\bigcirc$:2M2B of eggshell catalyst, $\bullet$:2M1B of eggshell catalyst, $\triangle$:2M2B of uniform catalyst, $\blacktriangle$:2M1B of uniform catalyst).

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Fig. 11 shows a result of Pd metal distribution from EPMA of the catalysts obtained after different impregnation time (a)time =0.5h, (b)time = 1h, (c)time =3h, (d)time =6h, (e)time =12h, and (f)time =24h.

Fig. 12 shows a variation of the thickness of Pd metal eggshell vs. impregnation time.

Fig. 13 shows a variation of the content of Pd metal vs. impregnation time.

Fig. 14 shows an EPMA spectrum of 0.2 wt% Pd/Al₂O₃ catalyst calcined at 500°C.

Fig. 15 shows a temperature programmed reduction (TPR) spectrum of 0.2 wt% Pd/Al₂O₃ catalyst calcined at various temperatures (a)300°C, (b)400°C, (c)500°C, (d)600°C, and (e)700°C.

Fig. 16 shows a plot of Pd metal distribution vs. calcining temperature of 0.2 wt% Pd/Al₂O₃ catalyst.

Fig. 17a & Fig. 17b shows an EPMA spectrum of metal distribution of Pd and Ni eggshell.

Fig. 18 shows an EPMA spectrum of Ni metal distribution; (a)5min, (b) 10min, (c)20min, and (d)40min.


Example 1: Effect of conversion efficiency, selectivity, and life of eggshell and uniformly distributed Pd/Al₂O₃ catalyst on isoprene selective hydrogenation

Step 1: Preparation of 0.2 wt% of Pd - uniformly distributed catalyst Pd/ Al₂O₃

0.1523g of Pd(NH₃)₄(NO₃)₂ having a Pd purity of 36.04 wt% were dissolved in 50ml of deionized water. To the obtained solution, 10.045g of δ-Al₂O₃ (spherical particles with diameter of 2mm, surface area of 82.4 m²/g, and pore volume of 0.570 cc/g) were added and then stirred with a shaker at 100 rpm for 3 hours. After filtration, the obtained solid was dried at 100°C for 1 hour and then treated by raising temperature from ambient temperature to 350°C at a rate of 10°C/min and maintained at 350°C for 6 hours.

The obtained catalyst sample has 0.2 wt% of Pd content from elementary

analysis and Pd distribution is uniform resulted from an EPMA analysis as shown in Fig. 1.

Step 2: Preparation of 0.2 wt% of Pd eggshell catalyst Pd/Al$_2$O$_3$

0.1068g of Pd(CH$_3$COO)$_2$ having a Pd purity of 47wt% were dissolved in 150ml of toluene. To the obtained solution, 25.048g of δ-Al$_2$O$_3$ were added and followed by the same treatment as described in step 1. The obtained catalyst sample has an eggshell distribution of Pd metal from an EPMA analysis as shown in Fig. 2.

Step 3: Activity test of catalyst

The activity test of both catalysts obtained from the above preparations was conducted in a system of downflow continuous fixed bed reactor with the selective hydrogenation of 10wt% isoprene in solvent n-heptane. The reactor was a vertical stainless steel tube with inner diameter of 2.2cm and inner volume of 94ml. The furnace was temperature-controlled by means of electric heating system and PID thermostat. The reaction product was maintained at -30°C as a condensed product by means of a freezing circulator and then sampled at a time interval for GC analysis of its composition. The mass equilibrium of greater than 97% showed that the system had no problem for reaction test. The operating conditions of reactions were as follows.

A. About 1g of catalyst mixed with 25ml of spherical glass beads having diameter of 0.4-0.6mm, were filled in a reactor. The top and the bottom of the reactor were further filled with the 0.4-0.6mm spherical glass beads.

B. 440 Psig of nitrogen was used for leaking test.

C. PdO on the catalyst was reduced to Pd at 100°C, 410 Psig and a hydrogen flow rate at 1.2(NTP)/h, which was maintained for 10 hours.

D. After the reduction was completed, temperature was decreased to a reaction temperature of 44°C and reactions were carried out at P=30atm, T=44°C, under a mass spacial flow rate =18h$^{-1}$(g of feed/h·g of catalyst), with H$_2$/Isoprene molar ratio =2.262.

E. The reaction system is simplified as the following:

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        ┌──────► 3M1B ──────┐
        │          ↓         │
        │          ↓         │
IP──────►  2M2B ──────────►IC5
        │          ↑         │
        │          ↑         │
        └──────► 2M1B ──────┘
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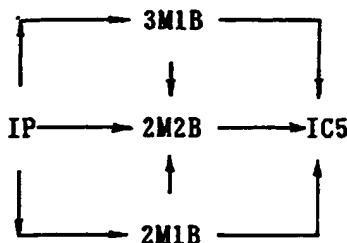
in which IP represents isoprene;

        3M1B represents 3-methyl-1-butene;

        2M2B represents 2-methyl-2-butene;

        2M1B represents 3-methyl-1-butene; and

        IC5 represents isopentane.


Isoprene was reacted by 1,2-hydrogen addition to generate partially hydrogenated products 2M1B and 3M1B. However, 2M2B could be formed by 1,4-addition via double bond shift isomerization of 2M1B and 3M1B, in which 2M1B and 2M2B were the main feedstock of TAME (tertiary amyl methyl ether) process. The undesired product IC5 was produced by a further hydrogen-addition saturation of isopentenes (abbr. as MB thereafter; representing a sum of 3M1B, 2M1B, and 2M2B).

Fig. 3(a) and Fig. 3(b) show that the concentration of the main products 2M1B, 3M1B, 2M2B, and IC5 depends upon the variation of time on stream in the hydrogenation of isoprene respectively with eggshell and uniform catalysts. Fig. 4 is derived from Fig. 3, in which the content of isoprene varies with the time on stream and a result that eggshell catalyst is endowed with a higher activity (i.e., conversion) and a lower decay rate of reactivity is obtained.

The spent catalyst of both types after being reacted were analyzed with DSC (differential scanning calorimeter) and the high molecular weight polymer harder coke of the spent catalyst were extrated with toluene and analyzed with a GC/mass after being concentrated. The result is shown in Fig. 5 and Fig. 6 and Table 1. In Fig. 5, the two types of catalyst show similar strong peak (represents softer coke) at a temperature of 308°C, and, weak peaks

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respectively appear at 408°C for eggshell catalyst and at 455°C for uniform catalyst represent the existence of harder coke. A retention time of GC of shorter than 20.4mm can be obtained from Fig. 6 and Table 1. Two types of catalyst have similar softer coke but only uniform catalyst has harder coke when the retention time is longer than 20.4 min. The evidence shown by the spectrum of DSC and GC/mass can make us understand why the eggshell catalyst is endowed with a lower decay rate of reactivity than the uniform catalyst.

The variation of concentration vs. reaction time on stream for the major product MB and the product IC5 of an over-saturated hydrogenation is shown respectively in Fig. 7 and Fig. 8. Obviously, eggshell catalyst is advantageous to produce more major product isopentenes and less undesired product isopentane.

The selectivity of isopentenes ($S_{MB}$) is defined as:

$$S_{MB} = \frac{\text{total moles of } (2M1B+2M2B+3M1B)}{\text{converted moles of IP reaction}} \times 100\%$$

Fig. 9 shwos the variation of $S_{MB}$ vs. reaction time on stream for the two types of catalyst. Obviously, eggshell catalyst has a higher selectivity of isoprene. As 2M1B and 2M2B are main feedstock of TAME process, Fig. 10 shwos the variation of the selectivity of major products 2M1B and 2M2B vs. reaction time on stream for the two types of catalyst. Again, eggshell catalyst has a higher selectivity of 2M1B and 2M2B than uniform catalyst has.

Summing up the above experimental results, eggshell catalyst is superior to uniform catalyst in conversion of isoprene, selectivity of isopentenes, and catalyst life for a selective hydrogenation of isoprene.

Example 2: Thickness of Pd-eggshell and Pd content controlled by impregnation time.

Step 1: Several 10g portions of δ-Al$_2$O$_3$ spherical support (with diameter of 4mm) were separately impregnated in 200ml of over-saturated Pd(CH$_3$COO)$_2$/toluene solution under stirring of a shaker at 100 rpm. The impregnation time for each portion of the support was controlled respectively to be 0.5, 1, 6, 12, and 24 hours. After filtration, the obtained solid was

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dried at 100°C for 1 hour and then treated by raising temperature from ambient temperature to 350°C at a rate of 10°C/min and maintained at 350°C for 6 hours.

Step 2: The obtained catalyst samples were analyzed by EPMA after different impregnation time. The measured Pd-metal distribution is shown in Fig. 11. Fig. 12 shows a plot of Pd-eggshell thickness (r/R) adopted from Fig. 11 vs. the impregnation time, in which the longer impregnation time causes the thicker Pd-eggshell thickness. Fig. 13 shows a plot of Pd wt% vs. the impregnation time and longer impregnation time causes higher Pd content.

Example 3: Pd dispersion on Pd-eggshell catalyst controlled by calcining temperature

Step 1: 0.534g of Pd(CH$_3$COO)$_2$ having a Pd purity of 47 wt% was dissolved in 750 ml of toluene. To the resulted solution, 125.24g of $\delta$-Al$_2$O$_3$ (spherical particles with diameter of 2 mm, surface area of 82.4 m$^2$/g, and pore volume of 0.570 cc/g) were added and then stirred with a shaker at 100 rpm for 3 hours. After filtration, the obtained solid was dried at 100°C for 1 hour.

Step 2: The dried catalyst sample was separated into five aliquot portions. Each portion was independently heated from ambient temperature to 300°C, 400°C, 500°C, 600°C, and 700°C at an elevating rate of 10°C/min and then maintained at final temperature for 6 hours. The resulted catalyst sample has 0.2 wt% of Pd content via elementary analysis and obtain a uniform Pd distribution on the outer layer of supports with a Pd-eggshell thickness (r/R) of about 0.05, which is not changed due to a variation of the calcining temperature, via EPMA analysis. The Pd content of catalyst sample calcinated at 500°C was quantitatively determined via 21 points of EPMA data and the result is shown in Fig. 14.

Step 3: About 0.300g of each catalyst sample resulted from different calcination temperatures were conducted with TPR by raising the temperature from 25°C to 300°C at a rate of 10°C/min under a gas flow of Ar/H$_2$ with a molar ratio of 9:1 and at a rate of 30 cc/min. Opened the heated furnace after the temperature reached 300°C and then a TRS (temperature resolved

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sorption) was conducted with quenching. The amount of hydrogen via chemisorption at higher adsorption temperature and via absorption at lower temperature on bulk Pd was measured [see J. of Catal., 96, (1985) 51]. The Pd-metal dispersion is calculated from the following equation:

$$D = Ac/(Ac+2.8Aa)$$

where   D represents dispersion,

Ac represents peak area of $H_2$ chemisorption, and

Aa represents peak area of $H_2$ absorption (bulk).

The spectrum resulted from TPR and TRS experiments of each catalyst sample is shown in Fig.15. The Pd metal dispersion is calculated from TRS spectrum and is plotted versus the variation of the calcining temperature as shown in Fig. 16. Obviously, the Pd metal dispersion decays as the calcining temperature increses.

Example 4:    Preparation of catalyst with linear decrease of Pd metal distribution from outer layer toward spherical core

Step 1: $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in deionized water to form a solution of 1M concentration. Spherical $\gamma$-$Al_2O_3$ (with diameter of 4mm, surface area of 173 $m^2/g$, and porous volume of 0.760 cc/g) was placed in the solution and treated by wet impregnation for 1 hour. Filtered and dried at 110°C for 1 hour.

Step 2: The resulting catalyst sample was placed in a solution of over-saturated $Pd(CH_3COO)_2$/toluene and treated by wet impregnation for 0.5 hour. Then, filtered and dried at 110°C for 1 hour.

Step 3: The resulting catalyst sample was subject to an EPMA analysis for determination of Ni and Pd metal distribution. The obtained spectrum is shown in figure 17. Obviously, the Pd metal distribution exhibits a linear decrease from outer layer toward spherical core while the Ni metal distribution is uniform.

Example 5: Preparation of catalyst by controlling Ni eggshell thickness with impregnation time

Step 1:  $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in THF solvent to make a solution of 3.0M concentration. Each of an impregnation solution was made by impregnating

1 0

1g of spherical support γ-Al$_2$O$_3$ (with diameter of 2mm, surface area of 173m$^2$/g, and porous volume of 0.760 cc/g) in a 5cc of the above Ni-containing solution. The impregnation time was controlled to be 5min., 10min., 20min., and 40min, respectively. Filtered and dried at 120°C for 12 hours.

Step 2: The resulting catalyst sample was subject to an EPMA analysis for determination of Ni metal distribution. The obtained spectrum is shown in figure 18. Obviously, the longer of the impregnation time, the thicker of the Ni eggshell thickness.

It can be seen from the foregoing that a new method is disclosed for preparing supported metal catalysts with eggshell active metal profile. The inorgano- or organometallic compounds, preferably comprising Pd, Ni, Co, Mo, Cu, Pt, Fe, Ag, Ir, Pb, Ti, Sn, V, and Zn, etc. are dissolved in an organic solvent, such as benzene, toluene, xylene, methanol, ethanol, and tetrahydrofuran (THF), etc. and/or an organic solvent mixture thereof. The catalyst precursors (ie. the reactive metal of the prepared organic or inorganic metal concentrated solution) are carried to the surface of MgO, Al$_2$O$_3$, SiO$_2$, TiO$_2$, ZrO$_2$, zeolite, active carbon, and polymer support by wet impregnation and/or spray method. The metal concentration profile and metal loading can be precisely controlled by choosing suitable solvent and/or operation conditions.

Table 1 : Detailed Composition of Coke Precursor of Eggshell and Uniform Catalysts

| Coke Precursor | Uniform Catalyst | | Eggshell Catalysts | |
|---|---|---|---|---|
| | R.T. (min) | R.A.$\neq$ | R.T. (min) | R.A.$\neq$ |
| 1. 2,4-dimethyloctane | 13.058 | 0.936 | 13.139 | 1.000 |
| 2. 1,2-dimethylbenzene | 14.702 | 0.172 | 14.753 | 0.361 |
| 3. 5-(1-methylvingl)-1,3 cyclopentadiene | --- | --- | 15.020 | 0.299 |
| 4. benzaldehyde | 17.631 | 0.859 | 17.663 | 0.812 |
| 5. propylbenzene | --- | --- | 18.018 | 0.100 |
| 6. 1-ethyl-2-methylbenzene | 18.228 | 0.311 | 18.260 | 0.374 |
| 7. 1,3,5-trimethylbenzene | 18.507 | 0.156 | 18.532 | 0.179 |
| 8. 1-methylethylbenzene | 18.915 | 0.115 | 18.942 | 0.114 |
| 9. 1,2,4-trimethylbenzene | 19.455 | 0.898 | 19.479 | 0.734 |
| 10. biscyclo[2,2,1]heptyl-2,5 diene-7-ol | 20.222 | 0.627 | 20.237 | 0.222 |
| 11. 1-methyl-5-(1-methylethyl) cyclohexane | 20.316 | 0.655 | 20.332 | 0.363 |
| 12. 1,2,3-trimethylbenzene | 20.496 | 0.138 | --- | --- |
| 13. 4-methylphenol | 20.928 | 0.152 | --- | --- |
| 14. unknown | 25.217 | 0.224 | --- | --- |
| 15. 4,5-dimethyl-1-hexene | 26.052 | 0.188 | --- | --- |
| 16. 4,5-dimethyl-1-hexene | 26.334 | 0.438 | --- | --- |
| 17. 4,5-dimethyl-1-hexene | 26.906 | 1.000 | --- | --- |
| 18. unknown | 27.465 | 0.168 | --- | --- |
| 19. unknown | 30.807 | 0.232 | --- | --- |
| 20. 3-methyltridecane | 31.014 | 0.361 | --- | --- |
| 21. 3-methyltridecane | 33.426 | 0.221 | --- | --- |
| 22. 3-methyltridecane | 34.107 | 0.512 | --- | --- |
| 23. unknown | 34.217 | 0.303 | --- | --- |
| 24. 4,5-dimethyl-1-hexene | 35.119 | 0.574 | --- | --- |
| 25. unknown | 36.071 | 0.872 | --- | --- |
| 26. unknown | 36.246 | 0.172 | --- | --- |

$\neq$ R.T. : Retention time ; R.A. : Area ratio of coke precursor obtained from GC-Mass.

## Claims

1.      A process for the preparation of an eggshell-shaped
catalyst for use in selective reduction or oxidation, the
process utilising an organo- or an inorgano-metallic compound
and comprising the steps of:

    (a)   dissolving the metallic compound in an organic
solvent selected from aromatics, alcohols and a mixture
thereof at an ambient temperature or by heating;

    (b)   carrying the active metal from so prepared solution
of the organo- or inorgano-metallic compound to a support
comprising at least one of $Al_2O_3$, $SiO_2$, zeolite, $TiO_2$, $ZrO_2$,
MgO, active carbon, polymers, or a mixture thereof, by wet
impregnation or spraying, and controlling the impregnation
time or the concentration of the solution, so that an
eggshell-shaped metal catalyst with a controlled thickness of
the metal eggshell and metal content is obtained; and

    (c)   further calcining the obtained catalyst at a
selected calcination temperature or temperatures to control
the metal dispersion.


2.      A process according to claim 1, wherein the metallic
compound comprises Pd, Ni, Co, Mo, Cu, Pt, Fe, Ag, Ir, Pb, Re,
Ti, Sn, V or Zn.


3.      A process according to claim 1 or claim 2, wherein the
inorganic solvent is selected from toluene, benzene, xylene,
methanol, THF and a mixture thereof.

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4.   A process according to claim 1, wherein the organometallic compound is Pd $(CH_3COO)_2$; the Pd $(CH_3COO)_2$ over-saturated or suitable concentrated solution is made by dissolving in toluene; the support is $Al_2O_3$; the impregnation time is from 0 to 48 hours; the thickness of the Pd metal on $Al_2O_3$ support is from 0 to the radius of a whole support; and the Pd content of the obtained Pd metal is from 0 to 4.0 wt%.

5.   A process according to claim 1, wherein the supported catalyst has a linear decrease of Pd metal distribution from outer layer toward core of the support, characterised in that Ni metal is carried to $Al_2O_3$, support by wet impregnation with $Ni(NO_3)_2 \cdot 6H_2O$ aqueous solution, followed by impregnation with the organopalladinum solution according to the process of claim 2, whereby a catalyst containing two metals Pd and Ni with Pd distribution having a linear decrease from outer layer toward core of the support, while Ni is uniformly distributed, is obtained.

6.   A process according to claim 4 or claim 5, further comprising the step of calcining the obtained catalyst at 100°C-1200°C to control the dispersion of Pd metal.

7.   A process according to any one of claims 1 to 6, wherein the prepared catalyst having ununiform metal distribution is used in a reaction of selective hydrogenation or selective oxidation for a preferable selectivity and yield of the obtainable intermediate.

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8.    A process according to any one of claims 1 to 3, wherein the metallic compound is $Pd(CH_3COO)_2$.


9.    A process according to any one of claims 1 to 3, wherein the impregnation time is from 0 to 48 hours.


10.    A process according to any one of claims 1 to 3, wherein the thickness of the active metal on the support is from 0 to the radius of the support.


11.    A process according to any one of claims 1 to 3, wherein the active metal content of the obtained catalyst is from 0 to 4.0 wt%.


12.    A process for the preparation of an eggshell-shaped metal catalyst, substantially as herein described.

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|---|---|---|---|
| **Application No:** | GB 9603728.8 | **Examiner:** | John Warren |
| **Claims searched:** | 1 - 12 | **Date of search:** | 6 June 1996 |

**Patents Act 1977**
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

    UK Cl (Ed.O): B1E

      Int Cl (Ed.6): B01J 35/00,35/02,37/02

Other:   Online database: WPI

**Documents considered to be relevant:**

| Category | Identity of document and relevant passage | | Relevant to claims |
|---|---|---|---|
| X | GB 1,601,715 | ENGELHARD - see Example 1 and Claim 1 | 1 2 3 6 9 - 11 |
| X | GB 1,538,330 | DEUTSCHE-GOLD - see Examples 8 11 12 | 1 2 3 6 9- 11 |
| X | GB 1,440,789 | MITSUBISHI - see Example 2 | 1 2 |
| A | US 4,519,951 | UOP | |

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| X | Document indicating lack of novelty or inventive step | A | Document indicating technological background and/or state of the art. |
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